Rotational tunneling of NH_4 and NH_3D and dipolar interaction in $(NH_{3.6}D_{0.4})_2PtCl_6$[a)]

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At 10% deuteration ammonium hexachloroplatinate still exhibits the cubic phase $Fm3m$ of the protonated material at all temperatures. Rotational tunneling of the ammonium isomers NH_4^+ and NH_3D^+ was measured by neutron spectroscopy. At temperatures $T \geqslant 18$ K the energies and intensities of the observed tunneling transitions agree with a statistical occurrence of ammonium isomers and a cubic environment. Below $T = 18$ K there is no change of the NH_4 spectrum while the NH_3D transition adopts an unresolved broad intensity distribution before it transforms into a new structured low temperature spectrum. The intermediate spectrum is interpreted as fingerprint of a potential distribution of statistically distributed disordered NH_3D ions interacting by long-range dipolar coupling. The low-temperature spectrum finds an explanation as frozen minimum energy configurations of coupled NH_3D dipoles. A dipole moment of NH_3D of 0.05 D can be derived from the difference of tunnel splittings. © *2002 American Institute of Physics.*
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I. INTRODUCTION

Despite the already long-lasting activity in characterizing A_2BC_6 perowskites these model substances still attract significant interest. Rotational potentials of ammonium ions in $(NH_4)_2BC_6$ compounds, with B a tetravalent metal ion and C a halogen, have been systematically studied by neutron tunneling spectroscopy.[1,2] Ammonium hexachloroplatinate, $(NH_4)_2PtCl_6$, is a compound with the second largest tunnel splitting known in this class. The crystal structure of the protonated species is $Fm3m$ down to helium temperature. The tunneling sublevels are determined by the tetrahedral site symmetry of the ammonium ion. This leads to the well-known doublet in our case with transition energies $\hbar\omega_{A\to T} = 32\ \mu$eV and $\hbar\omega_{T\to E} \sim 1/2\hbar\omega_{A\to T}$. In terms of tunneling matrix elements this level scheme is described by a single parameter, the 120° overlap matrix elements h. The four possibly different h_i are identical by symmetry and the three 180° overlap matrix elements H_j are negligibly small.[3]

Due to its extreme sensitivity to changes of the rotational potential, tunneling has frequently been used to study disorder. In the case of the ammonium hexahalo alloys the ammonium ions have such large distances that replacing some of it by alkali ions of similar ionic radius affects the tunnel splitting very little:[4] the octopole-octopole interaction decays fast and the monopoles of the two ionic species determining the crystal field seem to be very similar.

Because of its large tunnel splitting $(NH_4)_2PtCl_6$ was a candidate to show the large isotope effect of rotational tunneling. However, $(ND_4)_2PtCl_6$ undergoes a phase transition at $T_c = 27.2$ K.[5] Its low-temperature crystal structure is supposed to be tetragonal $P4_2/n$,[6] while the isomorphous $(NH_4)_2PdCl_6$ transforms into monoclinic $P2_1/n$.[7] An understanding of the isotope effect may be obtained by approaching the fully deuterated material in smaller steps. For this purpose partially deuterated samples are used. Only at a critical deuteration c_D^* does the low-symmetry structure of the fully deuterated material appear. With further increasing the deuterium concentration the phase transition temperature increases until it reaches the value of the pure deuterated material. In the homologous Pd salt the phase transition is suppressed below $c_D^* \sim 0.3$.[8] Due to its lower T_c, $(ND_4)_2PtCl_6$ can be expected to show a higher critical concentration c_D^*. Thus the compound dealt with in this paper still crystallizes in the cubic structure $Fm3m$ at all temperatures.

Due to proton exchange and the low degree of deuteration, the predominant ammonium species are the spherical top NH_4 representing an electrical octopole and the symmetric top NH_3D with a dipole as lowest electrical moment. Tunneling spectra will be affected by the symmetry of the rotor due to their different multipole interactions with the surroundings. Since the isotopic species are chemically equivalent, NH_4 and NH_3D can be assumed to occupy sites statistically. Accordingly effects of disorder come into play. For partially deuterated ammonium hexachloropalladate[8] the qualitatively different temperature dependence of the NH_3D tunneling transition compared to that of the symmetric NH_4 was interpreted as the formation of a dipolar orientational glass at NH_3D sites due to its specific additional dipolar interaction. NH_4 is essentially insensitive to disorder due to

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the short-range octopole-octopole interaction. Whether tunneling of NH_3D in ammonium hexachloropalladate is of one- or three-dimensional character has been discussed recently by solving the three-dimensional low-symmetry eigenvalue problem.[9]

By investigating $(NH_4)_2PtCl_6$ which is isomorphous to $(NH_4)_2PdCl_6$ but easier to prepare we intend to find out whether dipolar coupling of partially deuterated ammonium ions is a general phenomenon. Ammonium hexachloroplatinate even can be grown as single crystals. Thus in addition to spectroscopy the subtle disorder may also be investigated in the future by diffraction like it is done in other cases.[10]

II. EXPERIMENTAL DETAILS AND RESULTS

A. Sample preparation

The sample preparation is based on $PtCl_2$ and ammonium chloride as starting materials. The problem with preparing A_2PtCl_6 with $A=NH_4^+$ or ND_4^+ is due to the lower stability of the oxidation state Pt^{4+} compared to Pt^{2+}. Only in an acid environment, i.e., when prepared under a flow of chlorine gas, does the synthesis lead to the required compound

$$PtCl_2+2NH_4Cl+Cl_2\rightarrow(NH_4)_2PtCl_6. \quad (1)$$

The degree of deuteration $c_D=0.1$ is adjusted by the appropriate ratio of protonated and deuterated ammonium chloride. The preparation of a well-defined sample is an important part of the experiment as can be seen from inconclusive data of an earlier attempt.[11]

B. Inelastic neutron scattering

1. Rotational tunneling

The energy range from -32 to 4 μeV was investigated using the high-resolution backscattering spectrometer BSS1 at the research reactor FRJ2 of Forschungszentrum Jülich, Germany with its Si-Ge monochromator. The incoming wavelength is $\lambda\cong6.27$ Å, the energy resolution $\delta E\sim1.8$ μeV. The accessible energy range contains all relevant tunneling transitions. The sample weight was 2.43 g. The flat container was adjusted to a beam size of 3×4 cm^2 and oriented at 45° to the incoming neutron beam. At such conditions the scattering probability of the sample was 13%. Due to additional absorption, the sample transmission was 70%. Typically, the measuring time was 24 h/spectrum. Ten spectra were recorded at temperatures $1.8\text{ K}\leqslant T\leqslant29.7$ K. A typical set of background-corrected spectra is shown in Fig. 1. The spectra represent the sum over the three detectors at large scattering angles from 90° to 150°. The average momentum transfer is 1.6 Å^{-1}.

Transition energies are obtained by standard fitting procedures. The scattering function[3] is composed of an elastic line and tunneling transition lines. The former is represented by a δ function, the latter by Lorentzians. Features evolving due to the unusual behavior of the NH_3D are phenomenologically represented by Lorentzians. The scattering function composed this way is numerically convoluted with the measured resolution function. Table I shows the extracted parameters. Due to overlapping lines, correlations of parameters may arise. To avoid unreliable results we attributed the same linewidth to all three tunnel transitions above 25 K. Below this temperature the width of the NH_3D line becomes a free fit parameter which accounts for its obvious broadening.

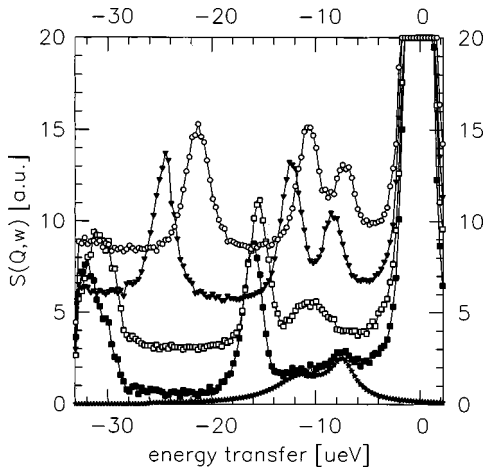

FIG. 1. Tunneling spectra of $(NH_{3.6}D_{0.4})PtCl_6$. Average momentum transfer 1.6 Å^{-1}. Sample temperatures $T=1.8$ K (■), 12.1 K (□), 25.9 K, (▼), and 29.7 K (○). Instrument: BSS1 of FZJ. The lowest line represents a decomposition of the NH_3D tunneling line at $T=1.8$ K into two broad contributions. See the text.

For comparison the spectrum of pure $(NH_4)_2PtCl_6$ was measured with the same setup of the spectrometer. At a temperature $T=1.8$ K a tunnel splitting of $\hbar\omega_{A\rightarrow T}=32.4$ μeV is obtained which is 5% larger than the equivalent line in the partially deuterated sample.

Below $T\sim8$ K the NH_3D line assumes a new shape. Two broad peaks at $\hbar\omega_t=7.5$ and 11.5 μeV emerge from the broad single line. In addition the intensity of the $T\rightarrow E$ transition 15 μeV increases slightly.

The fitted shifts and widths of tunneling lines are shown in an Arrhenius plot in Fig. 2. The shifts are related to activation energies of 6.2 and 6.9 meV for NH_4 and NH_3D, respectively. The broadening of the NH_3D line with decreasing temperature prevents a similar analysis of the linewidths.

TABLE I. Temperature dependence of the tunneling transition energies $\hbar\omega_t$ of NH_4 and NH_3D and the width Γ_1 of the NH_3D tunneling line of $(NH_{3.6}D_{0.4})_2PtCl_6$ and of fully protonated material.

	NH_4	NH_3D		
T [K]	$\hbar\omega_{A\rightarrow T}$ [μeV]	$\hbar\omega_1$ [μeV]	Γ_1 [μeV]	c_D
1.8	32.40	—	—	0.0
1.8	30.81	7.5/11.5	1.3/3.0	0.1
4.0	30.85	7.5/11.5		
8.3	30.87	8.9	2.59	
12.1	30.45	9.3	2.8	
15.3	29.70	10.0	1.25	
17.0	29.41	10.0	1.15	
18.5	28.66	9.91	0.99	
21.6	26.78	9.16	0.318	
25.9	23.70	8.03	0.216	
29.7	20.56	6.94	0.439	
E_S [meV]	6.2	6.9		

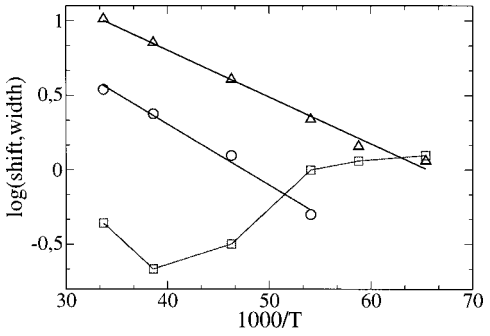

FIG. 2. Arrhenius plot of the shifts of the NH_4 (△) and NH_3D (○) tunneling lines and the width of the NH_3D line (□) vs temperature. Solid lines: linear regression. The derived activation energies are shown in Table I.

2. Librations

The excitations in the meV regime were measured using the new thermal time-of-flight spectrometer SV29 at the research reactor FRJ2 of Forschungszentrum Jülich, Germany.[12] The spectrometer was set up for an incoming wavelength $\lambda_i = 1.76$ Å and an elastic energy resolution of $\delta E = 1.7$ meV. Some characteristic modes at larger energy transfers were observed using $\lambda_i = 1.5$ Å. Here 2.8 g of powder material were used in a flat sample container of (25 $\times 50 \times 1$) mm^3 oriented at 45° to the incoming neutron beam. Partially deuterated samples were compared to fully protonated ones for two temperatures $T = 3.3$ K and $T = 40$ K. The samples differ only by the relative intensities of their characteristic energies (Fig. 3).

III. DISCUSSION

While the observations at high temperature ($T > 18$ K) fit well into the general understanding of rotational tunneling the partially deuterated rotors show unusual and interesting effects at low temperatures. Accordingly the discussion is split into three sections dealing with three characteristic temperature regimes.

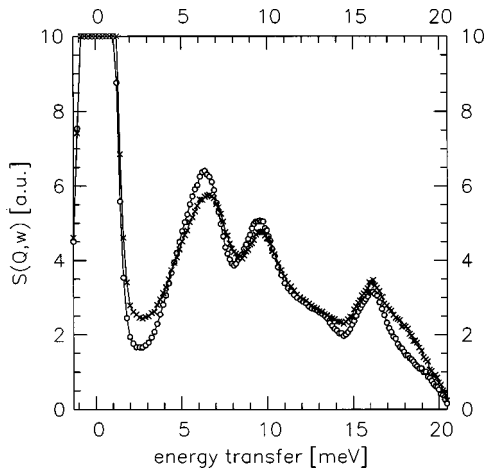

FIG. 3. Scattering function of $(NH_{3.6}D_{0.4})_2PtCl_6$ in the meV regime. Sample temperatures $T = 3.3$ K (○) and 40 K (×). Solid lines are guides to the eye. Instrument SV29 at FZJ.

A. High-temperature regime ($T > 18$ K)

1. Activation energies

The broadening of the tunneling lines with temperature is too weak to allow a quantitative interpretation. There are significant shifts, however. They result from coupling to phonons and can be described by Arrhenius laws (Fig. 2). According to the standard theory[13] the activation energy should be lower than or equal to the methyl librational mode E_{01}. Systematic errors affect the result only a little. In case of NH_4 there is an initial small increase of tunnel energies with increasing temperature followed by the usual line shift to lower energies. The increase is a sign of unusually strong coupling to phonons by a breathing term.[2,14,15] Only if the density of states below E_{01} is negligible will the activation energy for the line shift approach E_{01}. As is evident from the density of states (Fig. 3) this is almost the case for $(NH_4)_2PtCl_6$. Due to the anomalous behavior at low temperatures, only the four highest temperatures can be used to extract an activation energy for NH_3D. A fictitious low-temperature tunneling splitting is needed to get values for the line shifts. This quantity is obtained by scaling up the high-temperature value by the same shift factor found experimentally for the unaffected NH_4 groups. Keeping these difficulties in mind only shifts larger than 1 μeV were evaluated. This technique is the most reliable one of attributing librational modes to tunneling transitions. The activation energies are shown in Table I. They agree reasonably well with the energy of the more strongly temperature-dependent peak of the density of states (DOS) at 6.8 meV (Fig. 3). Thus, as expected, the presence of 30% NH_3D does not lead to a separated new librational band at the experimental energy resolution since the barrier is almost unaffected by the proton exchange.

2. Rotational potentials

Rotational excitations are interpreted within the model of single-particle rotation. In case of the three-dimensional NH_4 rotor the tunnel splitting is obtained from the tunnel matrix elements in the tetrahedral A_3 potential.[16] This symmetry is imposed by the crystal structure. The tunnel splitting of NH_4^+ in the partially deuterated material is reduced compared to the fully protonated material (Table I), indicating a small increase of the rotational potential. This can be explained by an increased octopole moment of ammonium ions containing a more localized deuteron. The stronger interaction leads to a larger potential with a smaller tunnel splitting. Quantitatively the relative change of the tunnel splitting by 1.9 μeV (4.5%) corresponds to a change of the barrier height by 1.4% or 0.3 meV.

NH_3D is treated as one-dimensional rotor. Thus its tunnel splitting is given by the solution of the Mathieu equation. Two excitations must be known to determine a rotational potential up to second order. The tunnel splitting $\hbar\omega_t$ is obviously the first one. We have to use its value extrapolated to helium temperature to be independent of a temperature effect. As a second mode we include the first librational energy E_{01}. Based on the temperature dependence of the tunneling line and the phonon spectrum the mode at 6.8 meV is as-

TABLE II. Potential barriers of NH_3D and NH_4 rotors as estimated from the tunnel splittings and E_{01}.

Species	$\hbar\omega$ [μeV]	E_{01} [meV]	Potential [meV]
NH_4	31.0/15.5		$A_3=55$
NH_3D	10.5[a]	6.8	$V_3=43.0$, $V_6=-22.0$
NH_3D	11.5	6.5	$V_3=43.0$, $V_6=-23.0$
NH_3D	7.5	6.8	$V_3=47.0$, $V_6=-24.0$

[a]The tunnel splitting at high temperatures is extrapolated to zero temperature on the basis of the temperature dependence of NH_4.

signed to NH_3D libration. This mode overlaps with the NH_4 libration. Chosing a pure $\cos(3\varphi)$ potential barrier height leads to a first librational mode that is significantly too high. Only the introduction of a strong sixfold term yields a consistent description. Its explanation is contained in the crystal structure. A look along a threefold axis of the tetrahedron shows that the shell of nearest chlorine atoms in 1/8 of the unit cell consists of three layers, two of threefold symmetry but rotated by 60° with respect to each other and a central ring of almost sixfold symmetry. This topology is the origin of a strong sixfold term in the rotational potential. It also leads to a large tunnel splitting of the first excited librational state. Finite energy resolution and dispersion of the librational phonon branches overlapping with the other phonons cause this doublet structure of the DOS to be unobservable. The results are given in Table II.

3. Intensities of tunneling transitions

A quantitative analysis of the spectral intensities is based on the established scattering functions of the three-dimensional tetrahedral NH_4 rotor and that of the one-dimensional threefold NH_3D rotor.[3] We deduce the ratio R of the measured intensities of tunneling lines:

$$R=\frac{I(15.5\ \mu\mathrm{eV})}{I(10.5\ \mu\mathrm{eV})}=\frac{p(\mathrm{NH_4})}{p(\mathrm{NH_3D})}\,\frac{\frac{4}{8}(1-j_0)\,\delta(\omega\pm\omega_{ET})}{\frac{2}{3}(1-j_0)\,\delta(\omega\pm\omega_t)}$$

$$=\frac{3}{4}\,\frac{p(\mathrm{NH_4})}{p(\mathrm{NH_3D})}. \qquad (2)$$

Since the structure factors of the two isotopic rotors are identical, they cancel and the ratio is valid for any momentum transfer. $p(X)$ is the occurrence probability of the species X. If the protons are substituted at random, the occurrence probabilities of the various ammonium isomers obey a binomial distribution function $p(n,c_D)$, and $p(\mathrm{NH}_n\mathrm{D}_{4-n})=p(n,c_D)$ in Eq. (2). The proton number density of a partially deuterated species then is $n\cdot p(n,c_D)$. This quantity is a measure of the overall intensities of the respective tunneling lines. For a degree of deuteration $c_D=0.1$ one calculates $R=1.7$. The ratio extracted from spectra of Fig. 1 at temperatures higher than $T=18$ K varies between 1.4 and 2.1. The precise value depends on whether the widths of the two transitions are coupled or not and on how the unresolved quasielastic component emerging with increasing temperature is described. Any line width Γ_{qel} between $1/2\Gamma_{inel}$ and Γ_{inel} (Ref. 2) can be argued for. The important result is, however, that irrespective of the data scatter the mean value confirms the presence of statistical isomers. Therefore, the model of one-dimensional rotation of the NH_3D species underlying Eq. (2) is supported, too.

B. NH_3D linewidths and dipolar glass state

In ammonium hexahalo compounds tunneling lines show little broadening with increasing temperature.[17] The astonishing observation in $(NH_4)_2PtCl_6$ concerns the NH_3D line which *broadens with decreasing temperature* below ~18 K. In the following we attribute this unusual behavior to the dipole moment of the NH_3D symmetric top. The dipole moment $\vec{p}$ can be assumed to be mainly due to an offset position of the molecule. For quantitative estimates we further assume that the NH_3D center of mass coincides with the crystallographic center of symmetry. By the corresponding separation of the centers of charges of the ammonium ion and the ionic lattice a dipole moment $\vec{p}$ is created which is the origin of a dipolar field $\vec{E}_1^{dip}=\vec{p}_1/r^3$. The energy of a second dipole in this field varies with its orientation,

$$W_p=-\vec{p}\cdot\vec{E}_1^{dip}, \qquad (3)$$

and adds to the rotational potential. For $|p|\sim 0.1$ D, W_p is about 20 K.[8] Here $\vec{p}$ always directs towards the deuteron position. For random orientation in the crystal frame this is one of the four space diagonals. The rotational potentials are affected in two ways: first by the change of interatomic distances, second by the relative orientations of neighboring dipoles.

If the central molecule is a NH_4, there is no displacement and no dipole moment. A former experiment[4] has shown that the large distance between ammonium sites makes the rotational potential rather insensitive to an exchange of ammonium by alkali ions. In the present case the most likely environment of NH_4 contains two NH_3D. The octopole-dipole interaction is sufficiently short range not to influence rotational tunneling. This explains that the fully protonated species is not affected by lowering the temperature. For a central NH_3D dipole, however, the situation is different. Considering again nearest neighbors only, trimers and tetramers of NH_3D show the highest probability. They modulate the rotational potential by long-range dipolar interaction according to Eq. (3). As long as the energy kT of the phonon bath is of the order of the dipolar energy W_p the dipole moments can fluctuate between all relative orientations. If the reorientational rate is fast compared to the inverse recording time for one spectrum, the measured data represent an average over all possible orientational configurations. Due to the long-range dipolar interaction, very many dipoles contribute to the rotational potential of the central NH_3D. The many possible orientational configurations of a dipolar cluster lead to a—likely Gaussian—distribution of rotational potentials in strength and orientation with a corresponding inhomogeneous line broadening. If the reorientational rate is as well slow compared to the tunneling frequency ν_t, a finite lifetime does not lead to additional broadening of the tunneling transitions. Infrared spectra of

the three energetically different N-D stretching modes of very weakly deuterated ammonium perchlorate[18] and other materials show that these conditions are mostly fulfilled.

In contrast to a real glass the dipolar sublattice is *dynamically* disordered on the timescale of data acquisition.

C. NH_3D spectrum at $T=1.8$ K

With lowering kT below the dipolar energy W_p, the dipoles will no longer average over the complete orientational phase space. The low-temperature spectrum characterizes the configurations of absolute energy minima. To quantify the arguments we simplify the problem and consider nearest neighbors only. In the cubic $Fm3m$ structure of $(NH_4)_2PtCl_6$ the ammonium ion is surrounded by an octahedron of six ammonium ions. To reduce the complexity further we replace the binomial distribution of ammonium isomers at $c_D = 0.1$ by a binary mixture of $\sim$60% NH_4 and $\sim$40% NH_3D. There are then 6% NH_3D monomers, 19% dimers, 32% trimers, 28% tetramers, etc. While all relative orientations are equivalent for NH_4 they differ energetically for pairs of NH_3D due to the relative directions of their dipolar moments [Eq. (3)]. If we choose a central NH_3D with its deuterium oriented along $\{\overline{111}\}$ a next NH_3D neighbor has one possibility to orient antiparallel along {111} or in the three others, but equivalent orientations with, e.g., $\vec{p}$ along $\{\overline{1}\,\overline{1}1\}$, $\{\overline{11}1\}$, or $\{1\overline{11}\}$. The respective rotational potentials will be different. Despite an almost infinite network of NH_3D ions we can identify a fine structure of two broad tunneling bands at 11.5 and 7.5 μeV. Their difference must be related to the dipolar energy and allows a guess of the NH_3D dipole moment. We assume that the octopole moments of NH_4 and NH_3D are identical. In a roughest approximation we identify the difference in potential strengths with the additional dipolar interaction energy. We get $W_{\vec{p}} \sim 4$ meV from Table II. For the ammonium-ammonium distance of $\sim$5 Å, Eq. (3) yields a dipole moment of 0.05 D. This is in rather good agreement with the original estimate based on a geometry where the NH_3D center of mass coincides with the ideal lattice site, e.g., {1/4, 1/4, 1/4}.

IV. CONCLUSION

Rotational tunneling spectroscopy gives access to the rotational potentials of the spherical and the symmetric tops NH_4 and NH_3D in partially deuterated ammonium hexachloroplatinate. The tunnel splitting is found to be a sensitive and exact probe of weak changes of the environment. The unusual temperature dependence of rotational tunneling spectra of NH_3D is attributed to long-range dipolar interaction of NH_3D defects randomly distributed on ammonium sites.

Above $T \sim 18$ K a shift to smaller energies and broadening of tunneling lines with increasing temperature is observed for both NH_4 and NH_3D. As in most systems this is due to coupling to phonons.[13] For NH_4 this coupling to phonons can account for the observation in the full temperature range. In contrast to NH_4 the NH_3D spectrum exhibits a fine structure with decreasing temperature. NH_3D is sensitive to a larger environment because of the long-range dipolar interaction. At intermediate temperatures $12 \leqslant T$ [K] $\leqslant 18$ when kT equals about the dipole-dipole interaction energy of NH_3D ions a net dipolar term contributes to the rotational potential. Deuterium jumps make this term fluctuate. The complete orientational phase space is explored within the time of recording a spectrum, yielding the inhomogeneously broadened line of a dipolar glass phase. The separation into two discrete broad tunneling bands at the lowest temperatures $T \leqslant 12$ K is interpreted as condensation into configurations of lowest free energy. The number of transitions and their intensities can be related to NH_3D clusters with different relative orientations of dipole moments. Cluster formation is assumed to shield the dipole interaction by the formation of higher-order multipoles. A net dipole moment of 0.05 D is extracted from the splitting of the two tunneling bands. The value fits well with the assumption that the ammonium center of charge (symmetry) is displaced since the NH_3D center of mass coincides with the ideal lattice site.

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